HYDROCRACKING WITH NEW SOLID ACID CATALYSTS: MODEL COMPOUNDS STUDIES.

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Two new solid acid catalysts have been prepared by supporting zinc chloride on silica gel and acid-exchanged montmorillonite. The acid properties of these catalysts were determined by Hammett indicator method which showed that highly Bronsted acidic sites were present. SEM/EDS studies indicated a uniform distribution of silicon, zinc, and chlorine in the silica gel-zinc chloride catalyst. The activities of these catalysts in the hydrocracking of bibenzyl, polybenzyl, alkylbenzenes, and other heteroatom substituted aromatics were investigated. Products from these reactions were analyzed by GC/FTIR/MS/AED and are consistent with an ionic or acid-catalyzed mechanism. High conversions to benzene and other small molecular weight products depend not only on the presence of strong acid sites but also on the ability of the catalyst to promote hydrogenation of complexed cationic intermediates, rather than condensation to oligomeric or polymeric (retrograde) materials. Our results with model compounds account for the effectiveness of these solid acid catalysts for conversion of coals to lower molecular weight materials.

Key words: Depolymerization, solid acid catalyst, hydrocracking

INTRODUCTION

New concepts are required in designing catalysts for coal liquefaction to produce distillate fuels with a low content of heteroatoms such as sulfur, oxygen, and nitrogen. In a two stage process, heteroatoms are removed by catalytic hydrotreatment of high molecular weight coal liquids produced in a preliminary low-severity process. The preparation and use of strong acid-catalysts and superacids are active areas of research for isomerization, cracking, hydrocracking, alkylation, acylation, methanol to gasoline, etc. (1). Because of the reported advantages of the solid acid catalysts (2), recent research has focused on the preparation and characterization (2-6) of stronger acid catalysts.

Although molten zinc chloride effectively depolymerizes coals (7,8), significant hydrodesulfurization of aryl sulfur compounds is not effected with this reagent (9). Other disadvantages of zinc chloride are its difficulty of recovery and corrosive nature. In a recent paper we reported a solid catalyst prepared by supporting zinc chloride on silica gel to be effective in hydrodesulfurization of diphenyl sulfide and dibenzothiophene(10). In this paper we report the preparation and characterization of solid acid catalyst prepared by supporting zinc chloride on acid-exchanged montmorillonite. The catalytic hydrotreatment of bibenzyl, polybenzyl, cumene, 1-phenyldecane, and n-hexadecane with silica gel and acid-exchanged montmorillonite supported zinc chloride, and acid-exchanged montmorillonite catalysts is being reported here.

EXPERIMENTAL

Reagents

Bibenzyl, cumene, 1-phenyldecane, n-hexadecane and zinc chloride were obtained from

Aldrich. Montmorillonite was obtained from Clay Spur, Wyoming and purified as reported (11).

Preparation of Polybenzyl:

Dichloromethane (200 ml) was placed in a three necked round bottomed flask (500 ml) fitted with three septa, one for the nitrogen inlet syringe needle, a second for the nitrogen outlet syringe needle (oil bubbler), and third for injecting the reactants. The flask was flushed with dry nitrogen, and 40 ml of stannic chloride was injected into the flask. Freshly distilled benzyl chloride (40 ml) was added to the flask with occasional stirring. After the addition was over, the reaction mixture was allowed to age at room temperature for four hours. At this stage the reaction mixture was quenched by slowly (dropwise) adding ice-cold methanol. When the reaction subsided, 200 ml more of ice-cold methanol was added. A yellow viscous solid was formed. The cloudy supernatant liquid was poured off, and the precipitate was washed several times with ice-cold methanol, dilute NaOH, deionized water, and methanol. The resulting solid was dissolved in a minimum amount of dichloromethane and freeze dried. The dried polymer was redissolved in a minimum amount of tetrahydrofuran by adding a large volume of methanol. The precipitate was filtered, washed with methanol and dried in vacuo.

Preparation of Catalysts:

Preparation of acid-exchanged clay (AM): Sodium-exchanged clay (5.0 g) was suspended in 200 ml of 0.1N HCl and stirred for three hours. The acid washed clay was separated by centrifugation, and washed with deionized water until free of chloride ions. The resulting clay was air dried. Final drying was accomplished by heating the clay at 250°C until constant weight was achieved.

Silica gel and acid-exchanged montmorillonite supported zinc chloride catalysts were prepared as described earlier (10). Total acidity and pKa's of the catalysts were determined by n-butylamine titrations using Hammett indicators (12).

Analytical procedures; Instrumentation:

Carbon, hydrogen, and nitrogen analyses were performed on Control Equipment Corporation Model 240XA Elemental Analyzer. The method of Vogel (13) was used for chlorine analysis. Proton and ^{13}C NMR spectra were obtained in d_2-dichloromethane with TMS as standard on a Varian XL200 NMR spectrometer. Infrared spectra were recorded in KBr on either a Perkin Elmer Model 283 spectrophotometer or a Nicolet 20SXB FTIR spectrometer equipped with a mercury cadmium telluride (MCTA) detector, and a Nicolet 1280 computer with a fast Fourier transform coprocessor.

Weight averaged molecular weight determination was performed in THF by gel phase chromatography (GPC, Waters Associates Liquid Chromatograph Model M6000) on a triple column (microstyrogel) system calibrated with polystyrene and aromatic standards in the molecular weight range 34,500 to 202 and with UV detection.

Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped with J&W 60 m x 0.25 mm (i.d.), 1.0 micron DB-1701 capillary column. n-Octadecane was the internal standard. Isotope dilution GC/MS was performed on a Finnigan 800 ITD ion trap detector with an HP 5890A gas chromatograph and a J&W 30 m x 0.32 mm (i.d), 1.0 micron film of DB-5. Phenol, naphthalene, and tetralin were determined with the per-deutrated analogs as the respective internal standards. A 15 m x 0.25 mm (i.d.), 0.25 micron DB-5 film capillary column was used for the analysis of high boiling components.

Hydrocracking reactions:

In a typical run, 1.0 g of substrate and 0.5 g of the desired catalyst were placed in a tubing bomb (12 ml microreactor). The microreactor was evacuated, pressurized with 1000 psig of hydrogen, and placed in a rocking autoclave heated to 350°C. The heating continued for three hours. At the end of the reaction period, the microreactor was cooled to room temperature, degassed, and opened. The desired amount of internal standard was added to the product slurry, the product slurry was transferred into a centrifugation tube by washing with methylene chloride, and the solid catalyst was removed by centrifugation. The liquid sample was analyzed by gas chromatography/flame ionization detection (quantitative) and gas chromatography/Fourier transform infrared spectroscopy/mass spectrometry/atomic emission spectroscopy (14).

For the reaction of polybenzyl, the microreactor was attached to a series of three pre-weighed traps that were cooled in air, dry ice-acetone, and liquid nitrogen. The microreactor was slowly heated (3°C/min) to 250°C and held at this temperature until distillation stopped. The distillate was weighed, and dissolved in 10 ml methylene chloride. This solution was mixed with appropriate internal standards and analyzed by GC/FID, isotope dilution GC/MS, and GC/FTIR/MS/AED. The undistilled product was extracted with THF and separated into THF-soluble and insoluble fractions. Both these fractions were vacuum dried, weighed, and analyzed by FTIR, elemental analysis, and m.w. determinations.

Results and Discussion:

Elemental analysis of zinc chloride supported on silica gel (SZC) and acid-exchanged montmorillonite (AMZC) suggests a high loading of zinc chloride on the support surface. Most of the chlorine is present as zinc chloride (Ca. 98%), and only a small amount of chlorine (<3%) is present as M-O-Zn-Cl. SEM/EDS studies indicated a uniform distribution of silicon, zinc, and chlorine in the silica gel-supported zinc chloride catalyst (10). In this paper we prepared another catalyst by supporting zinc chloride on acid-exchanged montmorillonite. The pKa's and total acidity of silica gel-zinc chloride, acid-exchanged montmorillonite-zinc chloride, and acid-exchanged montmorillonite were determined by n-butyl amine titrations using Hammett indicators, and results are presented in (Tables 1 and 2).

TABLE 1

ACID STRENGTH ON CATALYST SURFACE

Catalyst	pka						
	-5.6	-8.2	-11.30	-11.99	-12.70	-13.75	-14.56
SZC	+	+	+	+	-	-	-
AM	+	-	-	-	-	-	-
AMZC-B	+	-	-	-	-	-	-

+ Color of the conjugate acid of a basic indicator appeared on the surface.
- The above color did not change.

TABLE 2

TOTAL ACIDITY BY AMINE TITRATION

Indicator	pka	Amount of Acid (mmole/g)		
		SZC	AM	AMZC-B
m-Nitrotoluene	-11.99	0.71		
p-Nitrotoluene	-11.30	0.97		
Benzalacetophenone	-5.6	1.96	1.28	1.55

The total number of moles adsorbed using amine titration was based on the benzalacetophenone as an indicator (all acid sites with strength up to pKa = -5.6 were determined). Due to the brown color of acid-exchanged montmorillonite -zinc chloride catalyst, the detection of color change was difficult. Therefore, this catalyst was mixed with silica gel-zinc chloride with a known acidity prior to titration with n-butyl amine. These titrations indicate that silica gel-zinc chloride catalyst has the greatest number of acid sites, and acid-exchanged montmorillonite the fewest. Comparison of the total amount of acidity for silica gel-zinc chloride catalyst using benzalacetophenone (pKa = -5.6), p-nitrotoluene (pKa = -11.3), and m-nitrotoluene (pKa = 11.99) indicated a decrease in the total acidity as the pKa of the of the indicator changed from -5.6 to -11.3.

The acid strength for the three catalysts, as determined by the amine titration, is provided in Table 1. For the silica gel zinc chloride the acid strength Ho lies between -5.6 and -12.7 (-5.6<pKa<-12.70). Acid-exchanged montmorillonite, and acid-exchanged montmorillonite-zinc chloride have acid strength Ho ≤5.6. Comparing the results of the acidity measurements of the three catalysts it appears that silica gel-zinc chloride is most acidic among the catalysts investigated.

Catalytic hydrocracking of model compounds:

In order to understand the nature and extent of catalytic activity of supported zinc chloride, reactions of bibenzyl, cumene, 1-phenyldecane, and n-hexadecane were investigated. All reactions were carried out with or without solvent in the presence of 1000 psig molecular hydrogen at 350°C for three hours. The catalyst-to-substrate ratio was 0.5. Percent conversion, which is a measure of the aryl-carbon bond cleavage, was calculated on the basis of the starting material reacted. The results are given in Table 3 as product yields (mmoles) and percentage conversion of the substrate to the products.

TABLE 3

CATALYTIC HYDROCRACKING OF MODEL COMPOUNDS
(1000 psig H_2 pressure, 350°C, 3 hrs, catalyst wt/substrate wt = 0.5)

Catalyst (g)	Substrate (mmoles)	Solvent (mmoles)	Conv. (%)	Major Product (mmoles)
none	BB (5.49)	none	1	toluene (trace)
SZC (0.50)	BB (5.49)	none	85	benzene (3.35) ethylbenzene (3.26)
*SZC (0.50)	BB (5.49)	none	70	benzene (3.14) ethylbenzene (3.03)
SZC (0.50)	BB (5.49)	p-Cresol (18.52)	37	phenol (2.27)
SZC (0.50)	p-Cresol (9.44)	none	80	phenol (2.04)
AM (0.50)	BB (5.49)	none	75	benzene (4.89)
AMZC (0.50)	BB (5.49)	none	66	benzene (3.96)
SZC (0.50)	Cumene (8.33)	none	99	benzene (1.84)
SZC (0.50)	1-Phenyldecane (4.59)	none	40	benzene (0.65) C_1-C_6 benzenes
SZC (0.50)	n-Hexadecane (4.42)	none	20	C_3-C_6 alkanes

* = aged catalyst
BB = bibenzyl

A blank reaction of bibenzyl (without catalyst) gave almost complete recovery of the starting material, and only a trace amount of toluene was detected. No benzene or ethylbenzene were observed in the products. However, when bibenzyl was reacted with zinc chloride supported on silica gel, 85.5% of bibenzyl was converted into smaller molecules. The major products from this reaction were benzene, toluene, and ethylbenzene. Small amounts of propylbenzene, butylbenzene, tetralin, benzylethylbenzene, benzylpropylbenzene, etc. were also formed. No chlorine from the catalyst was found to be incorporated into the organic products. The catalyst was recovered in almost quantitative amounts, and the chlorine contents were the same as in the starting catalyst. The amount of coke or polymeric material in the recovered catalyst that could have been formed due to acid-catalyzed retrograde condensation reaction was negligible, and no corrosive melt was formed. In a reaction with aged catalyst, lower conversion (70%) of bibenzyl was observed. Aging, or perhaps

exposure of the catalyst to atmospheric conditions may have changed the nature of the acidity of the catalyst (10).

Although this catalyst gave high conversion in the absence of solvent, a suitable solvent may be necessary for this catalyst to be useful for the coal liquefaction. Reaction of bibenzyl in p-cresol (solvent) was investigated. In contrast to the neat reaction, the conversion was low (37%) in this solvent. In addition, only 39% p-cresol was recovered at the end of the reaction. Bibenzyl gave the same major and minor products as in the reaction without solvent, but in much smaller amounts than expected. Bibenzyl substituted cresol, tetralin, naphthalene, anthracene, naphthol, and mono, and dimethylbibenzyl were some of the products. In order to understand the role of the solvent in the cleavage reactions, p-cresol was reacted with this catalyst and hydrogen under the same reaction conditions as those used for bibenzyl. Reaction of the solvent alone resulted in 80.4% conversion of cresol to other products. Only 27% of the expected phenol was formed. Dimethylphenols and phenoxyphenol were some of the other products of this reaction. The high reactivity of cresol eliminates it from consideration as a solvent. Under strongly acidic conditions, it apparently condenses extensively to high molecular weight products. Solutes also would become involved in these condensations.

In order to further demonstrate that the Bronsted and/or Lewis acidity was responsible for the reductive cleavages of aryl-methylene bonds, reactions of bibenzyl were also carried out with acid-exchanged montmorillonite and acid-exchanged montmorillonite supported zinc chloride. These reactions gave 75 and 66% conversions for acid-exchanged montmorillonite and acid-exchanged montmorillonite supported zinc chloride, respectively. A majority of the product was benzene, and small amounts of toluene, o-xylene, and ethylbenzene were also formed. In addition, almost 40% of the product was polymeric material, mainly polybenzyls. The origin of this polymeric material may have been acid-catalyzed polymerization of the benzyl species formed during initial stages of the reaction. Because of formation of the condensation products from the hydrotreating of bibenzyl with these catalysts, their effectiveness in hydrotreating coal liquids might be questioned. With regard to avoiding extensive condensation reactions, the zinc chloride supported on silica gel is most effective. Nevertheless, the zinc chloride supported on acid-exchanged montmorillonite gave respectable conversions in the hydrotreating of low severity liquefaction products from Wyodak subbituminous coal (15).

Although the conversions were high, the product yields are suggestive of the fact that only one aryl-methylene bond is cleaved under the reaction conditions employed. In order to further understand the mechanism of this reaction, iso-propylbenzene (cumene) was reacted with zinc chloride supported silica gel. This reaction gave almost complete conversion of the iso-propylbenzene, and benzene was the major product. The reaction of 1-phenyldecane with this catalyst gave 40.3% conversion. A large number of products were formed from this reaction. Major products were benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene and hexylbenzene, indane, etc.

Examination of the products obtained from the reaction of n-hexadecane with zinc chloride supported silica gel indicated 20% cracking to smaller molecules. Major products of this reaction being propane, butane, pentane, and hexane etc. The low conversion suggests that this catalyst may be useful for cleaving bonds attached to aromatic rings in coal macromolecules without unwanted cracking of alkanes to gases. No cracking of alkanes was observed when they were used as solvents for the model compound reactions.

In silica gel supported zinc chloride catalyst, highly acidic Bronsted sites are available due to the silica hydroxyls associated with zinc chloride. Protonation of the ipso position of the ring will give the arenium ion intermediate, which can

undergo aryl-methylene bond cleavage. The presence of benzylethylbenzene, benzylpropylbenzene, etc. in the hydrotreating products is indicative of carbonium ion intermediates in the reaction of bibenzyl. Formation of a "surfacebound" carbonium ion is hypothesized to explain the lack of extensive condensation that might occur if free carbonium ions were formed. Since the reaction rate is much higher with secondary alkyl groups (cumene reaction), it is clear that the reaction proceeds rapidly whenever the cationic leaving group can be stabilized by α- or β-phenyl groups or alkyl groups, and more slowly or with extensive rearrangement when the leaving group is primary (1-phenyldecane reaction). It is clear that the acid catalyst is effective in cleaving aryl-methylene bonds at relatively lower temperature and without chlorine substitution or extensive condensation of carbonium ion intermediates.
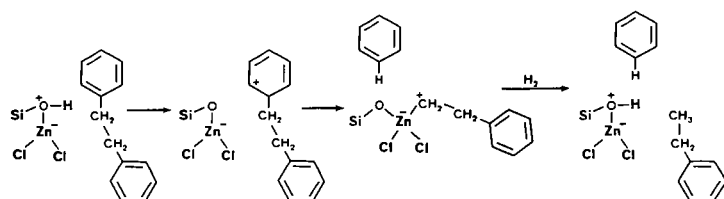

Figure 1. ACID-CATALYZED MECHANISM

Research is in progress to characterize the spent catalyst and to test the catalytic activity of the spent catalysts at higher temperatures.

Catalytic hydrocracking of model polymer:

Model coal polymers with well defined structures, thermally more stable than polystyrene or polybenzyl ethers, are needed for testing of hydrotreating reactions in order to understand the coal liquefaction. The synthesis of a model coal polymer, which meets the criteria of being highly branched, highly soluble, and thermally stable, has been accomplished. It was not clear from the literature that this is a bulky (branched) polymer; however, the thermal stability is good because of the methylene bridges between the benzene rings.

The infrared of the polymer showed a weak absorption in the 800-850 cm^{-1} range, corresponding to two adjacent hydrogens on an aromatic ring. This indicates that the para substituted benzene components of the polymer structure are relatively minor, probably less than 10%. Because of the intense absorption at 740 to 760 cm^{-1}, corresponding to monosubstituted benzenes, the structure must be highly branched containing many (90%) benzyl groups attached to the backbone system. A weak absorption at 900cm^{-1}, corresponding to single hydrogens on an aromatic ring, was also present in the spectrum. This absorption is usually weak, thus there are still some unsubstituted aromatic positions in the backbone system. The highly branched structure explains the high solubility of the polymer in organic solvents. NMR evidence shows that there are anthracene groups, but no chloromethyl groups.

The anthracene is undoubtedly formed by oxidation of dihydroanthracene by the stannic chloride. Although the formation of dihydroanthracene terminates the chain in terms of obliterating the electrophilic chloroethyl groups, the reaction of additional benzyl groups on the polymer can occur at any point. Thus, the

anthracene may not necessarily be on the end of the chain. Calculation of a molecular weight, based on the 1 to 23 ratio of anthracene to benzyl, gives a value of 2250 per anthracene unit. The weight average molecular weight was found from the GPC data to be 1300 daltons. The presence of anthracene units in the polymer will, however, delay the elution of the polymer substantially and cause a severe error in the GPC determination, which is based on the calibration with polystyrene.

The hydrotreating of polybenzyl (C, 92.96; H, 6.98; H/C ratio, 0.9) with zinc chloride supported on silica gel and 1000 psig hydrogen at 350°C for 3 hours gave 61% distillate. The distillate was found to consist of 95% benzene, toluene, oxylene in approximately equimolar amounts. Small amounts of cyclohexane methylcyclohexane, C_3 and C_4 benzenes, naphthalene, indane, tetralin, methylnaphthalenes, and anthracenes were also present in the distillate.

Mass balance and infrared analysis of the THF-soluble fraction indicated a small amount of polymeric material (6.9%) present. THF-solubles (Vacuum bottoms, C, 89.5; H, 6.21; H/C ratio, 0.83) were 32.9% of the starting polymer. Detailed characterization of the THF-soluble fraction is in progress.

This experiment demonstrates that the silica gel-zinc chloride catalyst is effective in depolymerization of highly branched alkylbenzene polymers without extensive condensation to insoluble chars.

ACKNOWLEDGEMENT

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